EFFECT OF FE-GA PAIRS DISSOCIATION AND ASSOCIATION PROCESSES ON RECOMBINATION LIFETIMES IN MULTICRYSTALLINE SI SOLAR CELLS

Marwan Dhamrin, Koichi Kamisako, Tadashi Saitoh
Tokyo University of Agriculture and Technology, 2-24-16 Naka-machi, Koganei, Tokyo 184-8588, Japan
Oliver Schultz, Stefan Glunz, ISE, Heidenhofstrasse 2, 79110 Freiburg, Germany,
Takeshi Eguchi, Teruhiko Hirasawa and Isao Yamaga, Dai-ichi Kiden Co., Chofu, Tokyo 182-0034, Japan

The recombination properties of Fe-Ga pairs in Ga-doped multicrystalline silicon wafers is investigated by means of effective lifetime measurements using quasi-steady-state photoconductance (QSSPC) and deep level spectroscopy (DLTS) techniques. A procedure to calculate active Fe concentrations in Ga-doped mc-Si wafers is developed based on the recombination parameters obtained from this study. The effect of Fe-Ga association and dissociation on solar cell output characteristics is simulated using PC-1D and experimental prove is given. In addition, the diffusion coefficient of iron in Ga-doped mc-Si is measured by monitoring the re-pairing effective lifetime decay as function of time.

Keywords: Ga-doped, Fe-Ga pairs, iron, silicon, lifetime

1 INTRODUCTION

Ga-doped mc-Si has become an important material for future solar cells due to its stability under illumination and its high carrier lifetimes [1]. Therefore, measuring the recombination parameters for this promising material is of great important specially of iron, the main defect in mc-Si. The primary technique for determination of interstitial iron concentration in p-type silicon is the analysis of change of lifetime as before and after dissociation of iron-acceptor pairs under the influence of thermal or optical activation. This procedure is a standard procedure in SPV, and can be used with some limitations (low injection level) by μ-PCD technique. Zoth and Bergholz pointed out that it is possible to determine the iron density by measuring the minority carrier diffusion length or the recombination lifetime, at low injection level, during the Fe-B state and then during the interstitial iron, Fe^+, state in B-doped wafers [2]. There technique was limited to the low injection level diffusion lengths measurement, which required a special sample preparation, a thick sample for instance. Recently, Macdonald *et. al* [3], applied high injection level lifetime measurement successfully to measure electrically active iron concentration in B-doped mc-Si by fitting the injection-level dependant effective lifetimes before and after activation to the SRH equation.

The same technique will be used in this work where the recombination properties of Fe-Ga pairs in Ga-doped multicrystalline silicon wafers will be investigated by means of effective lifetime measurements using the quasi-steady-state photoconductance (QSSPC) technique [4] and deep level spectroscopy (DLTS) [5]. In addition, a procedure to calculate active iron concentrations in Ga-doped mc-Si wafers is developed based on DLTS spectra and QSSPC effective lifetime fitting results.

2 RESULTS AND DISCUSSION

2.1 Measuring iron concentrations in Ga-doped silicon wafers

Similar to B-doped silicon, at room temperature, iron is mostly found to exist in the form of Fe-Ga pairs. After a proper activation, the Fe dissociated from the Fe-Ga pairs diffuses interstitially in silicon and resides on interstitial sites before relaxing to its equilibrium concentration. The association and dissociation processes by thermal annealing or optical activation of the Fe-Ga pairs are investigated by means of effective lifetime measurement.

In order to study the recombination parameters of Fe-Ga pairs, deep-level transient spectroscopy (DLTS) were performed. The DLTS scan is shown in Figure 1 where energy levels of E_V+ 0.3eV, for Fe-Ga pairs, and E_V+0.38eV, for interstitial Fe^+ were found. However, the cross capture sections obtained using the intercept at $1000/T=0$ from the Arrhenius plot of $ln(\tau_e T^2)$ versus $1000/T$ should be viewed with caution due to the high uncertainty.

On the other hand, normal fitting of the QSSPC data to the SRH lifetime will not give an accurate estimation for the defect energy level, however such fitting will result in good accuracy for electron and hole cross capture sections. Therefore, using the combination of DLTS and QSSPC to obtain the recombination parameters of Fe-Ga pairs will lead to more accurate results.

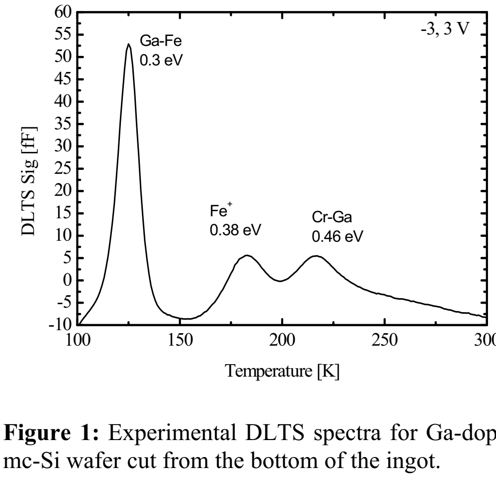

Figure 1: Experimental DLTS spectra for Ga-doped mc-Si wafer cut from the bottom of the ingot.

As shown in Figure 2, the effective lifetimes were fitted to the SRH lifetimes using the defect energy levels obtained from DLTS measurement. The fitting was performed simultaneously where both curves before and after activation were fitted according to a percentage of activated/non activated states. The solid lines represent the fits to SRH lifetimes with the parameters appears in Table 1. The fitting of the after dissociation data results in electrically active iron concentrations of 1.2×10^{11}cm^{-3} in addition to Fe-Ga pairs concentration of 3×10^{10}cm^{-3}.

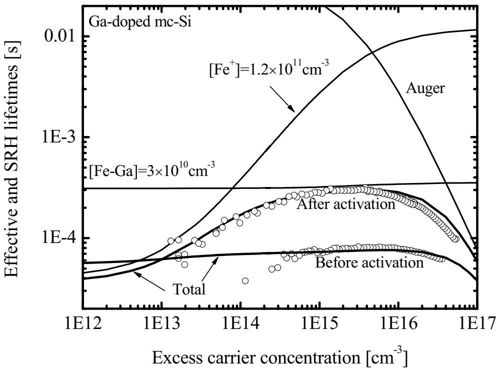

Figure 2: IDLS measurement, symbols, of Ga-doped mc-Si wafer before and after Fe-Ga dissociation.

Table 1: Summary of the Fe-Acceptors recombination parameters as a result of this work.

Defect structure	Energy level (DLTS)	σ_n[cm^{-2}]	σ_p[cm^{-2}]
Fe-Ga	E_v+0.30	4.96×10^{-13}(DLTS) 1.10×10^{-14}(IDLS)	5.6×10^{-14} (IDLS)
Cr-Ga	E_v+0.46	2.04×10^{-13}(DLTS)	
Fe$^+$	E_v+0.38	2.02×10^{-14}(DLTS)	

The recombination parameters including the energy levels of Fe-Ga and interstitial iron obtained from the combination of the DLTS and injection-level dependant lifetime spectroscopy (IDLS) measured by QSSPC are summarized in Table 1.

By using these recombination parameters, one can simulate the SRH lifetimes before and after activation to give better understanding of the Fe-Ga pairs effect. From the calculated SRH lifetimes, shown in Figure 3, the Fe-Ga pairs found to be a very active recombination center. Even at high resistivities, the active recombination nature of the Fe-Ga pairs is still dominant. The unique crossing point around injection levels of about 10^{14}cm^{-3} in B-doped SRH lifetimes before and after Fe-B dissociation described by Macdonald *et. al* [3] was not found in Ga-doped SRH lifetimes before and after Fe-Ga dissociations due to the different defect nature and position in the band gap.

Similarly to B-doped silicon wafers, it is possible to determine the iron density by measuring the effective lifetime during the Fe-Ga state and then during the interstitial iron, Fe$^+$, state in Ga-doped silicon wafers using the following equation

$$N_{Fe_{total}} = A.\left(\frac{1}{\tau_{SRH,Fe-Ga}} - \frac{1}{\tau_{SRH,Fe^+}}\right), \qquad (1)$$

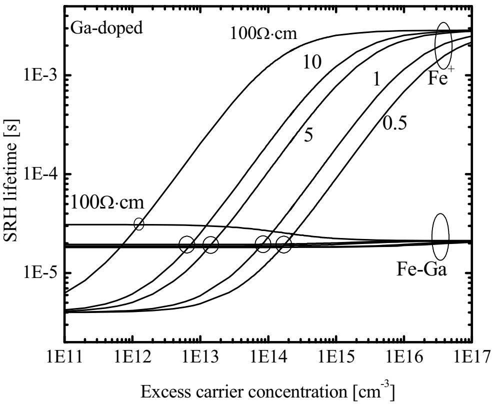

Figure 3: Recombination lifetimes of Ga-doped silicon before and after dissociation of Fe-Ga pairs at different resistivities.

where A is pre factor depends on the dopant density N_A, the excess carrier concentrations Δn, the carrier densities, n_1 and p_1, and electron and hole cross capture sections, σ_n and σ_p, respectively, of Fe-Ga and intestinal Fe$^+$.

$$1/A = \left[\frac{N_A + \Delta n}{\sigma_{p,Fe-Ga}(n_{1,Fe-Ga} + \Delta n) + \sigma_{n,Fe-Ga}(N_A + p_{1,Fe-A} + \Delta n)}\right] - \left[\frac{N_A + \Delta n}{\sigma_{p,Fe^+}(n_{1,Fe^+} + \Delta n) + \sigma_{n,Fe^+}(N_A + p_{1,Fe^+} + \Delta n)}\right] \qquad (2)$$

Figure 4 illustrates the inverse calculated values of the pre-factor A as a function of excess carrier concentration for different resistivities. The calculations show that the effective lifetimes will exhibit and increase after Fe-Ga activation even at low injection levels for resistivities above 5Ω·cm.

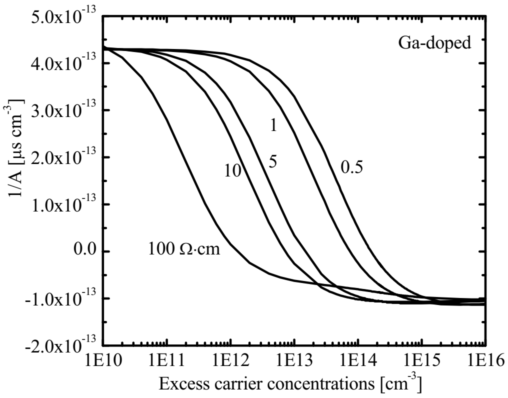

Figure 4: the pre-factor A calculated using Eq. 2 at different resistivities. The Calculation parameters were taken from Table 1.

B-doped and Ga-doped ingots were grown using the same thermal growth profile. The resulted dopant densities were different in both ingots. The electrically active iron concentrations were measured using the QSSPC after optical activation.

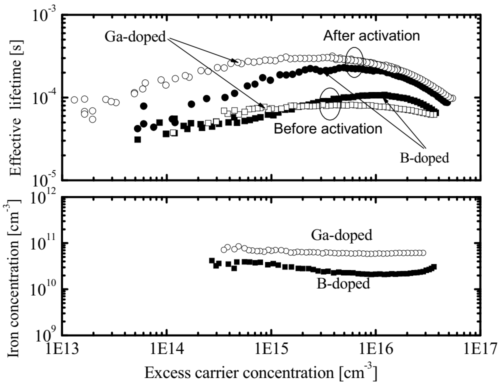

Figure 5: a) Recombination lifetimes of Ga-doped and B-doped silicon wafers before and after dissociation of Fe-Ga and Fe-B pairs and b) Iron concentrations calculated using the recombination lifetimes of Ga-doped and B-doped silicon wafers before and after dissociation of Fe-Acceptor pairs.

Figure 5 shows two experimental results of the carrier lifetime before and after iron-acceptor pairs activation in Ga-doped and B-doped wafers cut from the center of the ingots. The measurement was performed under high injection level to avoid any trapping effect might alter the measurement. The iron concentrations in both samples are indeed very close due to the same parameters used during ingot solidification. The results give another evidence to confirm the electron and hole cross capture sections obtained by fitting the injection level dependent lifetime to the SRH lifetime. The iron concentration in B-doped material was calculated using the parameters obtain by Macdonald *et. al* [3].

2.2 Effect of iron-acceptor association and dissociation on solar cell performance

The association and dissociation processes are extremely active under illumination in both B-doped and Ga-doped materials. The iron-acceptor pairs dissociate under light causing a small amount of degradation to the solar cell efficiency. Even though the process is reversible in dark, after illumination, such property still alters the solar cell performance and its characteristics output stability.

To establish better understanding about the Fe-Ga pairs dissociation and association effect on silicon solar cell efficiency, PC-1D simulation was performed using the calculated SRH lifetime before and after activation of Fe-Ga pairs. The solar cell were simulated by a simple n^+p solar cell structure using the calculated carrier lifetimes of Fe-Ga and Fe^+ at low injection levels. The calculations were performed using the batch mode with τ_n and τ_p as an input parameters at different iron concentration using the SRH statistics. The emitter, n^+, sheet resistance set to be 100Ω/□. In addition, 10% front reflectance and 1Ω/cm^2 series resistance were assumed. The surface recombination velocities were set to the values of 10000cm/s and 1000cm/s on front and back surfaces, respectively. In Ga-doped silicon wafers, the solar cell efficiency will be governed by the carrier lifetime of Fe-Ga recombination center. However, under illumination the solar cell will be governed by the carrier lifetime of the interstitial iron recombination center. It has been found that higher iron concentrations results in lower conversion efficiency. The relative changes of the solar cell open circuit voltage, short circuit current, fill factor and efficiency are shown in Figure 6. The effect of Fe-Ga pairs dissociation was noticeable and interested results were obtained. The relative change of the open circuit voltage will decrease with increasing the iron concentration at highly doped silicon wafers. However, at low doped wafers, an increase of the open circuit voltage will reach a maximum values before it drops again. The increased amount will vary according to the dopant density level. The relative change in short circuit current will drop with increasing the iron concentration for resistivities below 10Ω·cm whereas it will exhibit a little increase for higher resistivities. The over all efficiency drops with increasing iron concentration for resistivities below 3Ω·cm and will exhibit an increase for higher resistivities.

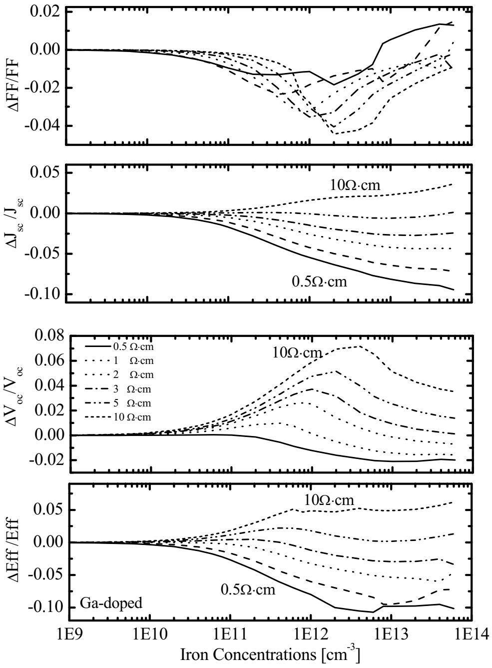

Figure 6: Relative changes of fill factor, short circuit current, open circuit voltage and conversion efficiency due to the activation of Fe-Ga pairs.

The simulation results of the Fe-Ga dissociation effect on solar cells output efficiency was experimentally confirmed using three different Ga-doped solar cells with different resistivities. As can be seen in Figure 7, the open circuit voltage improved after illumination due to the dissociation of Fe-Ga pairs and recovered again after annealing at 200°C with dark storage to insure complete pairing. In addition, the short circuit current was decreased with illumination resulting in over all efficiency decrease. The effect of resistivity was clearly noticed and agreed very well with the simulation results. However, similar results could not be obtained for B-doped solar cells due to the impact of light-induced defect generated during illumination which altered the measurement and have greater impact than that of Fe-B dissociation process.

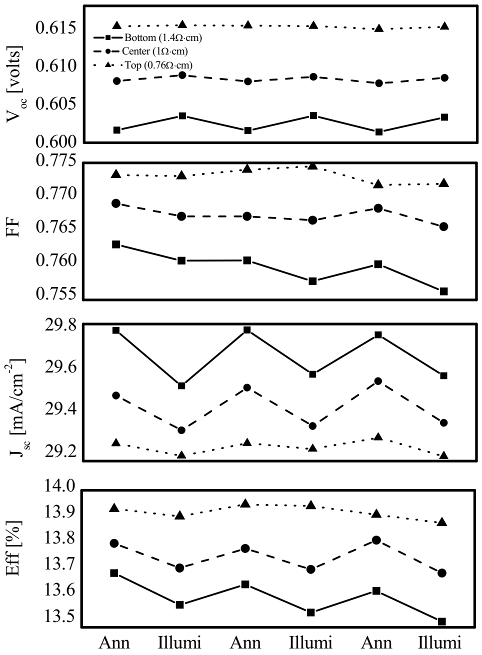

Figure 7: Experimental repetitive increase of V_{oc} after illumination and its decrease after annealing at 200°C with dark storage, decrease of *FF*, J_{sc} and *Eff* after illumination and its increase after annealing at 200°C with dark storage.

2.3 Iron diffusion coefficient

The effective carrier lifetimes measurement by QSSPC is an excellent technique to evaluate the iron diffusity in silicon due to its fast performance that allow an accurate time dependence estimation for the re-pairing process of activated iron-acceptor pairs.

In this study, Ga-doped wafer of 5Ω·cm was used to evaluate the diffusion coefficient in Ga-doped multicrystalline silicon wafer. After the complete dissociation, the increase rate of Fe-Ga pairs with time is equal to the of Fe^+ decrease rate with a decay time constant τ. This can be expressed by the following relation

$$\frac{N_{Fe-Ga}}{N_{Fe_{total}}} = .\frac{\left(\frac{1}{\tau_{a,t}} - \frac{1}{\tau_a}\right)}{\left(\frac{1}{\tau_b} - \frac{1}{\tau_a}\right)} = 1 - \exp(-t/\tau) \quad , \qquad (5)$$

where τ_a and τ_b are the carrier lifetimes before and after complete activation, $\tau_{a,t}$ is the carrier lifetimes after activation at a giving time during pairing. Using such a concept to measure the normalized defect concentration of the $N_{Fe\text{-}Ga}$ and N_{Fe+} concentrations, one can calculate the association time constant τ as fitted in Figure 8. From the measured time constant, the diffusion coefficient of Fe in silicon at room temperature can be calculated using the following equation:

$$D = \frac{\varepsilon_s \varepsilon_0 k_B T}{q N_A \tau}, \qquad (6)$$

where D is the diffusion coefficient of Fe, ε_s the dielectric constant, ε_0 the vacuum permittivity, k_B Boltzman's constant and T the temperature. The calculated diffusion coefficient for Fe in Si using Eq.(6) was 1.1×10^{-14} cm^2/s at 300K which is one order higher than the one calculated from ref[6], mainly B-doped silicon, 4.9×10^{-15} cm^2/s at 300 K. Interestingly, the results indicate a faster pairing for the electrically active iron in Ga-doped wafers. The reason might be the easy capturing of iron by the relatively bigger Ga atoms if compared to B ones.

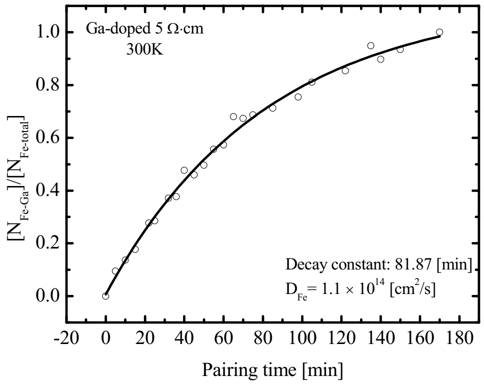

Figure 8: Association of interstitial Fe with Ga as function of relaxing time at 300K.

3 CONCLUSION

The recombination properties of Fe-Ga pairs in Ga-doped multicrystalline silicon wafers are investigated. Fe-Ga defect is lied above the valance band at E_V+0.3 and the electron and hole capture sections are 1.1×10^{-14} and 5.6×10^{-14} cm$^{-2,}$ respectively. Based on these recombination parameters, a procedure to calculate electrically active Fe concentrations in Ga-doped mc-Si wafers is developed. The effect of Fe-Ga association and dissociation on solar cell output characteristics is simulated using PC-1D and experimental prove to the simulated results is given. In addition, the diffusion coefficient of iron in Ga-doped silicon is measured by monitoring the re-pairing effective lifetime decay as function of time.

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